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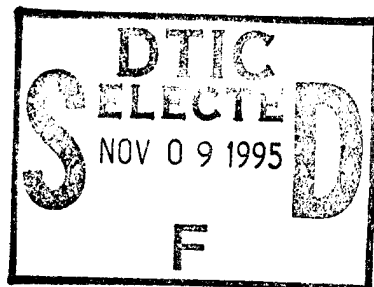F

TOUGHENING OF ANHYDRIDE CURED

EPOXY RESINS

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by

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TOUGHENING OF ANHYDRIDE CURED EPOXY RESINS

Abstract

Anhydride cured DGEBA epoxy resins are toughened
against crack propagation by incorporating functionally
terminated liquid butadiene-acrylonitrile rubber (CTBN).
Spherical domains of 2 - 3 μm diameter are formed in situ
during cure. With increasing amounts of rubber, the size of
the second phase particles decreases. Thermo-mechanical and di-
electric properties of the modified resins deteriorate rapidly
beyond 10% rubber content. The temperature, T_g, of the unmodified
system is 129°C; it drops to 126° with 10 parts rubber and to
119°C with 20 parts. The excess rubber appears to copolymer-
ize with the matrix resin. Also the coefficient of thermal
expansion increases disproportionately. The appearance and
growth of secondary relaxation peaks in the dielectric spectra
due to nitrile groups may be associated with the plasticizing
effect of the excessive rubber. Epoxy filled with liquid rub-
ber-treated silica powder shows a twofold improvement in frac-
ture surface work compared to untreated filler. An interaction
of the secondary amino groups of the ATBN (amine terminated)
rubber with the epoxy-silane coupling agent on the silica and
the epoxy resin appears to take place.

Background

     A well-known phenomenon which occurs with many rigid epoxy resin systems is cracking during mechanical or thermal cycling. This is more pronounced in glass reinforced resins or in resins being used as encapsulants for electrical components. In both cases, the epoxy is in contact with materials which have thermal expansion coefficients approximately 1/10 that of the resin. This large discrepancy creates stresses which cause cracks. In addition to providing paths for high voltage breakdowns, the cracks accelerate the infusion of environmental agents such as CO_2, moisture and oxygen. To avoid product failures because of this, many epoxies are flexibilized. Often the improved crack resistance is achieved at the expense of thermomechanical properties, however. For example, polyether-polyol is extensively used to plasticize epoxy resins but it has the disadvantages of:

    a) lowering the temperature, T_g, and hence the maximum allowable temperature from, say, 130°C to 75°C.

    b) increasing the coefficient of thermal expansion,

    c) impairing the dielectric properties of the resin system.

More attractive attributes of a good encapsulant are "stiff and tough" rather than "plasticized and tough."
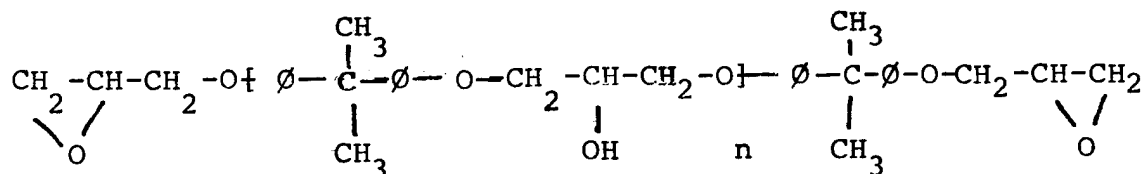
     Toughening of epoxy systems with liquid rubber additions has shown that crack resistance properties can be improved with little or no sacrifice of thermomechanical behavior. The thermal expansion and dielectric behaviors of the systems have not been studied, however, and such was the purpose of this work.

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The incorporation of small amounts of rubber as discrete particles in a glassy thermoset resin system can improve its crack resistance and impact strength. McGarry et al (1) were among the first to use liquid carboxyl terminated butadiene-acrylonitrile (CTBN) copolymers for this purpose. Siebert and Riew (2) described the chemistry of the in situ particle formation: the second-phase particle is a mixture of linear CTBN-epoxy copolymers and cross-linked epoxy resin. The morphology of the toughened epoxy systems was investigated by Rowe (3). Rowe and Riew (4) suggested deformation mechanisms based on shear bands or cavitation induced by the particles, when stressed. At low strains, the stress in the sample is borne largely by the rigid matrix and it is concentrated in the neighborhood of the rubber particles. As straining continues, the stress becomes more distributed among the rubber and the plastically yielding matrix. The rubber, now under tension, strengthens the deformed matrix and fracture is delayed, in favor of yield initiation elsewhere.

The experiments described above were concentrated on amine-cured epoxy resins, but the technology of rubber toughening should apply to anhydride cured resins also. In this report, we will show how the morphology of the CTBN-modified epoxy resin-anhydride systems relate to the thermo-mechanical and dielectric properties. An attempt has been made to improve the fracture toughness of silica filled epoxy resins by treating the silica powder with a coupling agent and a liquid rubber

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before the powder is incorporated into the resin.

Experimental

Epon 828: The liquid diglycidylether of Bisphenol-A

(DGEBA) resin is represented structurally as follows:

$$CH_2-CH-CH_2-O\{\ \emptyset-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\emptyset-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O\}-\emptyset-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\emptyset-O-CH_2-CH-CH_2$$

Where DGEBA of (n = 0)   = 87%

(n = 1)   = 10%

(n = 2,3)=   3%

Hycar CTBN: Low molecular weight carboxyl terminated

liquid copolymer of butadiene and acrylonitrile, repre-

sented chemically as below:

$$HOOC-\ [(CH_2-CH=CH-CH_2)_x\ -\ (CH_2-\underset{\underset{CN}{|}}{CH})_y]_m\ -COOH$$
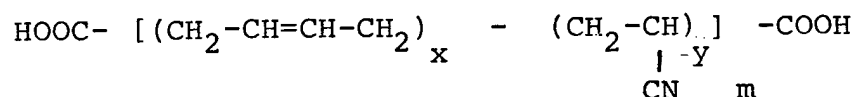
Where x = 5, y = 1, and m = 10

Lindride 14: Methyl-tetrahydrophthalic acid anhydride

(Lindau Chemicals)

Silica Filler: Silica powder of 15 μm particle size with

1% epoxy silane coupling agent from Union Carbide was used.

Formulation and Preparation of Test Specimens

        DGEBA resin : 100 parts (weight)

        CTBN 1300X8 copolymer: x parts with x = 0, 10 or 20

        Lindride 14: 80 parts

        DMP-30: 0.5 parts

Two hundred grams of Epon 828 and the x parts of CTBN were stirred in a beaker at elevated temperature until the mixture was clear. In another beaker, mix 160 gms. of cure agent Lindride 14 with 1 g. of accelerator DMP-30. Add this cure agent to the epoxy resin and stir the mixture for 5 - 10 minutes at 70 - 80°C. Pour the mixture into a Teflon-coated metal mold which has been preheated at 80°C. The mixture is pre-cured at 85°C for 6 hours and post cured at 120 °C for 6 hours. The pre-cure at the lower temperature helps reduce the shrinkage due to cure to $\leq$ 1%. In the case of silica filled formulations, 100 parts of liquid-rubber-treated silica per 100 parts of epoxy resin were used.

Test Specimen Machining

Each cured epoxy slab was machined into double cantilever beam test bars 1/4 in. x 1 1/4 in. x 8 in. long. The width of the samples was milled to 1.2 in.,and two 1/8 in. diameter holes were drilled at one end of the specimen, each 0.13 in. from the side edge and 0.14 in. from the end (Figure 1). The specimen was slotted in the center along its entire length on both sides. The slot dimensions were about 1/12 in. deep and

0.006 in. wide. A one inch long notch was cut through the
web portion of the specimen at the end containing the drilled
holes.

Fracture Energy Dtermination

The cantilever bars were tested in the Instron. Pins
were placed in the drilled holes of the specimen and the sample
was cleaved along the web, the machine operating at a constant
cross-head rate of 0.2 in. per minute. The fracture surface
work value of the specimen was determined by the use of the
force-distance plot and crack lengths. The results were as
follows:

Fracture surface work (γ) of unmodified resin: 0.26 $\frac{\text{in.lb.}}{\text{in.}^2}$

"   "   "   " resin with 10 parts CTBN:0.76 "

"   "   "   "   "   " 20   "   " : 1.42 "

Calorimetric Dilatometric Tests

Calorimetric studies were done with a Perkin-Elmer DSC;
dilatometric transitions were determined with a Perkin-Elmer
TMS-2. The glass transitions of the various formulations, as
determined at a 20°C/min. heating rate, were:

T_g of cured epoxy resin with no CTBN (A) : 129°C ,

T_g "   "   "   "   " 10 parts CTBN (B) : 126°C ,

T_g "   "   "   "   " 20 parts CTBN (C) : 119°C .

No residual cure was observed for these resins when scanned with

the DSC to higher temperatures.

The glass transitions measured with the Thermo-Mechanical Analyzer corresponded to the above T_g values when a lower heating rate of 10°C/min. was used. The thermal expansion coefficients of A,B, and C were measured in the temperature range of 50-100°C and, above T_g, in the range of 150-200°C (Figure 2). The results were as follows:

Coefficient of Thermal Expansion α (mm/mm/°C)

Samples	T_g	$\alpha_{50-100°C}$	$\alpha_{150-200°C}$
A	129°C	60×10^{-6}	174×10^{-6}
B	126°C	66×10^{-6}	185×10^{-6}
C	119°C	78×10^{-6}	205×10^{-6}

Scanning Electron Microscopy

After a sample had been tested for fracture energy, the cleaved surfaces were viewed with the S.E.M. With ten parts of CTBN, the particle size was approximately 3μm and with 20 parts, they were as small as 2μm. (Figure 3).

Dielectric Behavior

The temperature dependences of the dielectric constant and of the loss factor, tan δ, were observed in the temperature range of -120°C to 200°C at a frequency of 1 kHz. The relative dielectric constant showed the expected increase with increasing amounts of CTBN. For the anhydride cured resin alone, the relative dielectric constant remained low at about 3.4 up to about

120°C. Similarly, the tan δ showed a value of 0.005 over the same range. Both parameters were adversely affected by the presence of the CTBN, as can be seen in Figures 4 and 5.

Results and Discussion

Rubber modification of the anhydride cured epoxy resin improves its fracture toughness by a factor of 3 or 5.5, with 10 parts or 20 parts of liquid copolymer. Above 10 parts, the improvement in toughness is accompanied by a loss of thermo-mechanical and dielectric properties. The glass transition temperature, which is an indication of the maximum useful service temperature, shows a minor decrease with 10 parts of CTBN: the thermo-mechanical and dielectric properties are not seriously affected. Apparently most of the CTBN goes into the second phase, so there is little flexibilization. With greater amounts of CTBN, however, more of it copolymerizes with the epoxy, which results in flexibilization. This effect is manifested in the marked lowering of T_g when 20 parts of CTBN are used. The linear coefficient of thermal expansion is, in this case, already high before the T_g, and after the T_g, the thermal expansion increases by manyfold (Figure 2). Hence, with increasing amounts of CTBN, the service temperature of the epoxy system would be limited.

The dielectric properties of liquid rubber (CTBN) modified epoxy systems are very sensitive to the CTBN content (Figure 5). The appearance of a shoulder, and its proportional rise

with the CTBN content, near T_g in the dielectric spectrum of modified resin systems reinforces our assumption that the CTBN, beyond certain concentrations, acts as a flexibilizer. This "excess" CTBN, which is distributed in the epoxy matrix, possesses a high degree of mobility. We believe it is this mobility which gives rise to the β-relaxation in the tan δ curves at ca. -40°C. It should be possible to shift the distribution of CTBN in favor of the separated phase by changing the reaction parameters. By this, the T_g could be kept as high as possible, so the cured epoxy system with the higher CTBN content is both "stiff" and "toughened."

Another way of obtaining "stiff" and "toughened" epoxy systems would be to fill the resin with liquid-rubber treated silica powder. When ATBN-rubber was mixed with silica powder in a ball-mill for about 16 hours, an interaction between the epoxy-silane coupling agent on the silica powder and the amino group of the ATBN appeared to have taken place, as qualitatively evidenced by FTIR studies. The epoxy systems filled with ATBN-treated filler possessed a fracture toughness which was twice that of the unfilled epoxy systems. However, we believe that there is room for greater improvement in fracture toughness. With better mixing devices for the liquid rubber to interact with the silane coupling agent, the toughness of the filled epoxy systems is expected to increase.

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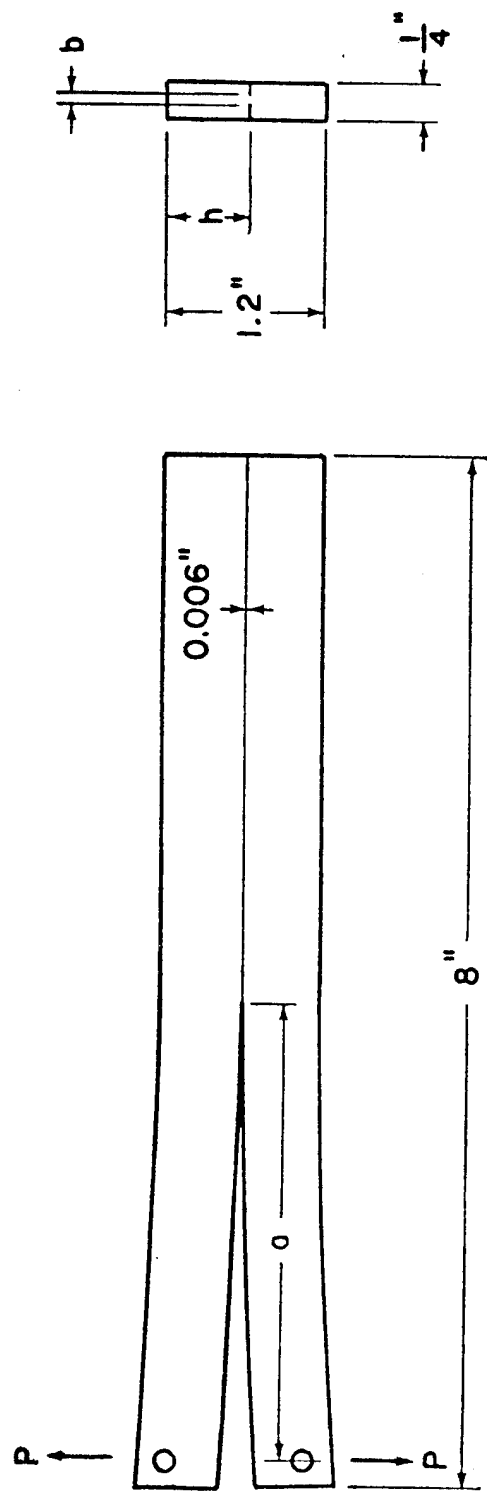
FIGURE 1.

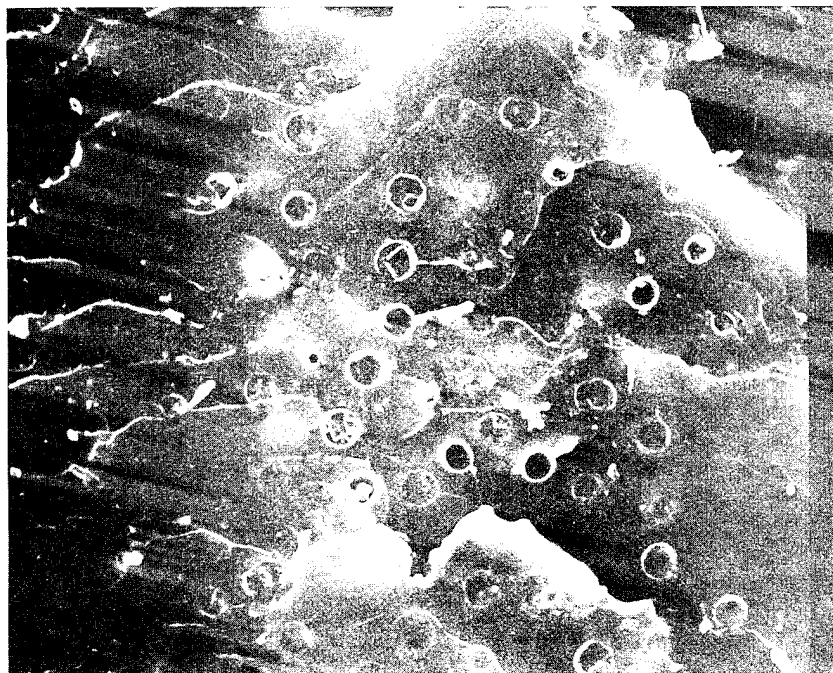DOUBLE CANTILEVER BEAM SPECIMEN.
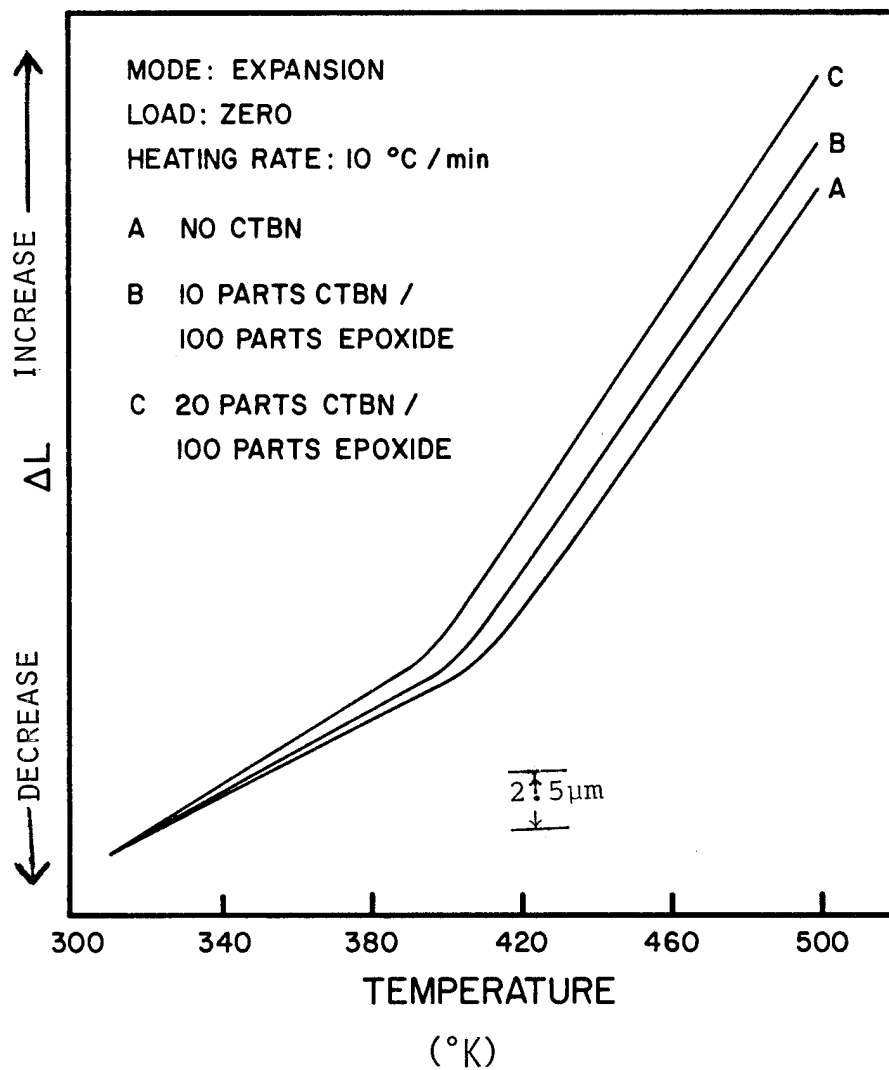
Figure 2. Linear expansion of epoxy systems with temperature.

(a)

(b)

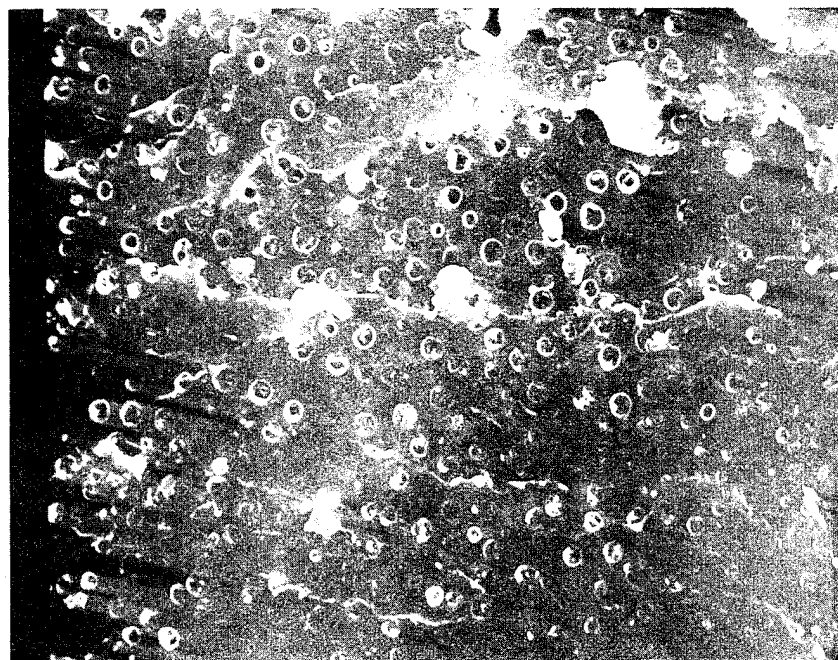Figure 3.   SEM OF CTBN-MODIFIED EPOXY SYSTEMS,
            (a) 10 PARTS CTBN AND (b) 20 PARTS
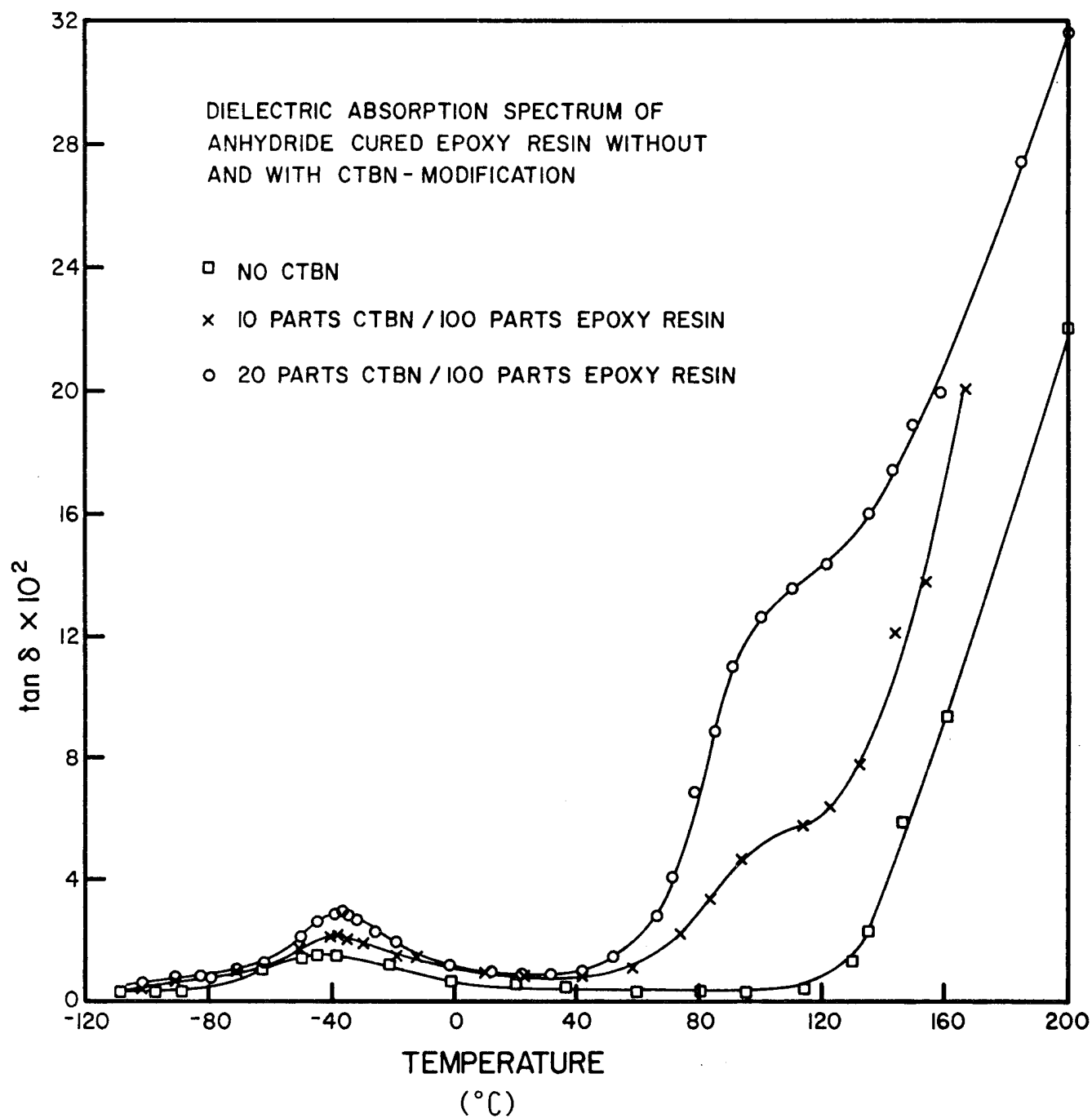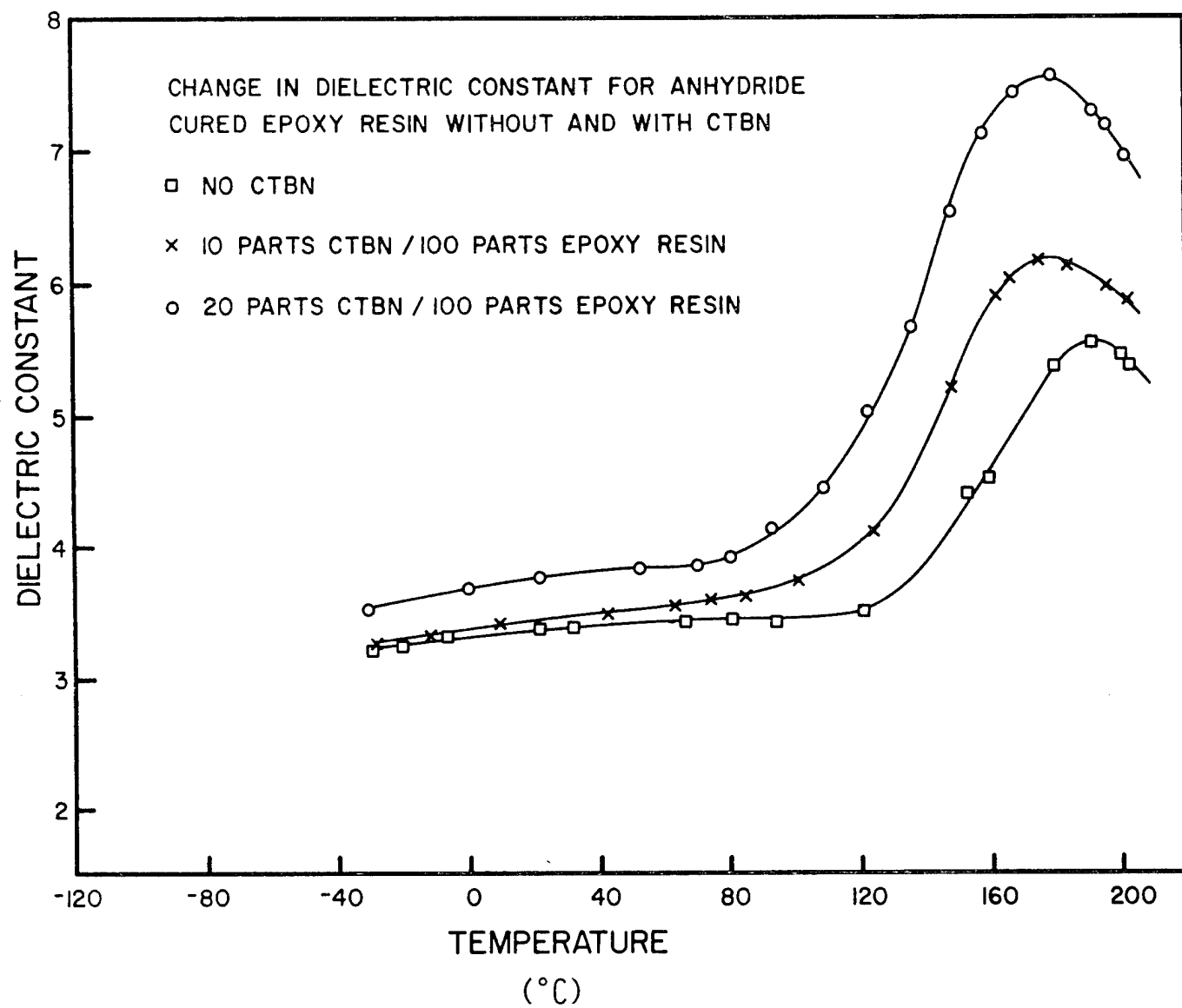   CTBN, MAGNIFICATION: 1000X.

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Figure 4

Figure 5